

MODELING $^{238}\text{U}/^{204}\text{Pb}$ (μ) AND INITIAL Pb OF LUNAR METEORITE NORTHWEST AFRICA 12593.

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Introduction: Apatite $\text{Ca}_5(\text{PO}_4)_3(\text{F}, \text{Cl}, \text{OH})$ serves as a valuable analytical resource. It is the only nominally hydrous phase on the moon and possesses the capacity to concentrate elements like U, Th, Pb, and rare earth elements (REE). This characteristic facilitates its use in U-Pb and Pb-Pb geochronology, allowing for the determination of the initial isotopic Pb and the $^{238}\text{U}/^{204}\text{Pb}$ ratio (μ) of the parent melt. In situ analysis of apatite grains can provide a detailed record of geochemical changes, revealing the broader petrogenetic and volatile history of the source material. This mineral is particularly informative in understanding the developmental history of its source. In situ analyses are crucial for lunar samples, predominantly composed of breccias, where correlating distinct grains with whole rock analyses poses challenges.

This study utilizes in situ apatite isotopic analysis of apatite grains in lunar meteorite Northwest Africa 12593 and model the initial Pb isotopic composition and $^{238}\text{U}/^{204}\text{Pb}$ (μ) of the source. We present in situ Secondary Ionization Mass Spectrometry (SIMS) Pb-Pb analyses of 12 apatite grains in Northwest Africa (NWA) 12593 to test two hypotheses: 1) NWA 12593 clasts and matrix are closely related and from the same source, and 2) the matrix material previously documented as having a highland affinity has a lower modeled μ than KREEP.

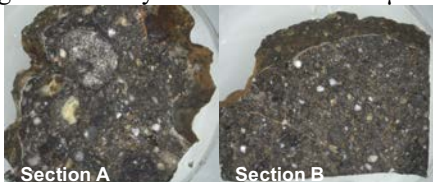


Figure 1: NWA 12593 slices were analyzed as part of this study. Photo credit: Carolyn Crow [2].

Northwest Africa 12593 Description: The lunar meteorite NWA 12593 is classified as a clast-rich fragmental breccia [1]. This breccia contains mineral fragments, and lithic clasts of basalt, granulite, and crystalline impact melt within a vesiculated impact-melt matrix with a highlands affinity (Fig. 1). Symplectite grains were identified with apatite and baddeleyite surrounded by pyroxene [2]. Previous studies have analyzed the Cl and H isotope composition of apatites from NWA 12593 [2,3]. Most grains have $\delta^{37}\text{Cl}$ ($\sim +20\%$), with a few grains exhibiting high $\delta^{37}\text{Cl}$ ($+45\%$ to $+55\%$) with high Cl concentrations [3]. δD values (-370% to $+1030\%$) are within the range of the low and high-Ti basalts in the Apollo collection [3].

Methods: The methodology consists of four steps: (1) identification of apatite via SEM, (2) using cathodoluminescence (CL) to identify zoning or regions of damage in the apatite grains, (3) SIMS analysis of Pb isotopes, and (4) initial Pb and μ modeling

Identification of Apatite Grains: Elemental maps were created using a JEOL IT500HR Field Emission Scanning Electron Microscope (FE-SEM) and ThermoFisher Pathfinder Energy Dispersive Spectrometer (EDS) at Southern Methodist University to identify zircon and phosphate mineralogies. Further point analysis via EDS of the phosphate grains was used to identify apatite vs other phosphates (e.g. merrillite). The SMU FE-SEM analyses were performed at a working distance of 10 mm and an accelerating voltage of 15 kV. Our study identified 66 apatites, 105 merrillites, 21 baddeleyites, and two zircons in section. While some apatite grains were $>100\ \mu\text{m}$, most were $<30\ \mu\text{m}$. The larger grains were targeted for our study.

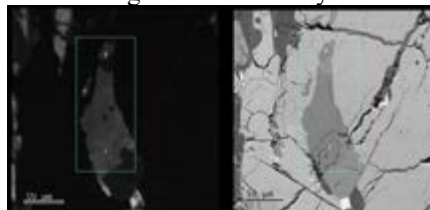


Figure 2: A S-rich apatite grain, which was located as an inclusion in a symplectite. Left: blue-filtered CL image of the grain. Notice the general lack of zoning but how some of the micro-cracks are visible. Right: IBSED image of this grain.

Cathodoluminescence (CL) imaging: Deformation of lunar apatite grains can lead to Pb loss, which in turn can yield ages younger than the sample's actual age [4]. While EBSD is a fantastic tool for quantifying crystal-plastic strain within grains, CL can highlight these deformed or recrystallized regions so that they can be avoided for isotopic analysis [4]. CL imaging also highlights any potential compositional zoning within the grains. Grains were imaged at Southern Methodist University using a Gatan Chroma2 CL detector, and large grains without noticeable deformation or recrystallization were selected (Fig. 2).

Pb-Pb SIMS Analysis: U-Pb isotope SIMS analyses were performed at the University of California, Los Angeles, using the CAMECA ims1290. Samples were analyzed with the Hyperion II ion source using a 5nA $^{16}\text{O}^+$ primary beam and $\sim 10\ \mu\text{m}$ spot size. SIMS spot

locations were chosen in each grain to avoid cracks or regions of potential deformation. Grains that potentially appeared zoned had two spots placed on the grain targeting the different zones. We analyzed twelve apatite grains ($n = 16$ spots) and two baddeleyite grain Pb isotopes. Grains that potentially appeared zoned had one spot placed in each subdomain or compositional zone.

Initial Pb and μ modeling: Unlike zircon and baddeleyite, Pb can readily substitute into apatite's structure during crystallization. The substitution of Pb within the apatite grain structure during formation presents a dichotomy; the initial Pb serves as a valuable geochemical marker while concurrently posing potential dating complications [5]. Furthermore, terrestrial Pb can contaminate samples.

Before modeling or calculating an age, the samples must be plotted on a Pb-Pb diagram, and contamination by modern terrestrial Pb must be identified (Fig. 3). Contamination by modern Pb creates a mixing line between terrestrial Pb and the grain's actual Pb-Pb value, creating higher values in $^{204}\text{Pb}/^{206}\text{Pb}$. Some studies correct this value by assuming that ^{204}Pb is terrestrial contamination, but that is problematic in the case of apatite grains, as apatite will incorporate Pb if available during crystallization. For this study, only the grains that did not form a mixing line with terrestrial Pb were modeled (Fig. 3). Therefore, ages were determined through ^{207}Pb - ^{206}Pb chronology [2,5] by identifying grains with negligible ^{204}Pb or using the ^{207}Pb - ^{206}Pb isochron method.

Finally, single-stage Pb growth curves were modeled for various μ values using a Pb isotope starting composition of Natan Troilite beginning at 4.5 Ga (Figure 3). The intercept of the array of grains with the modeled Pb growth curves yields the source μ composition. York linear regression was used to take into account for the correlated error between $^{207}\text{Pb}/^{206}\text{Pb}$ and $^{204}\text{Pb}/^{206}\text{Pb}$ ratios. A matlab code was written that calculates single stage μ and initial Pb values.

Results: This abstract focuses on pairing the chronology, see [2], with the initial Pb and μ models of the NWA 12593 apatite grains. Most grains cluster around 0.30 $^{207}\text{Pb}/^{206}\text{Pb}$ ratios and give a weighted average ^{207}Pb - ^{206}Pb age of 3493 ± 20 Ma (2σ) [2]. The oldest grain has a ^{207}Pb - ^{206}Pb age of 4334 ± 28 Ma (2σ). The age of 3493 ± 20 Ma was used to produce the paleogeochron. The oldest grain does not clearly form an array with any other grains, so unfortunately, its initial Pb cannot be modeled. At least one statistically significant population is identified that lacks terrestrial Pb contamination. The single-stage models yield μ values (470-600) depending on the starting time of the model.

Discussion: Within NWA 12593 are at least two groups of grains with unique ages and one with unique

μ values. The single stage μ results are higher than the modeled μ for ferroan anorthosite (8-35), lower than KREEP (~2000) [5,6]. They are consistent (470-600) with Apollo low and high-Ti basalts [5], also supported by the δD measurements[3]. It is difficult to compare these results to that of lunar anorthositic highland samples due to a lack of apatites in these samples [3]. These samples could be related to the Mg-Suite [6] based on the previously measured Cl isotope values and the modeled μ . Further comparison using trace element compositions, measurement of the Pb isotope ratio of the pyroxene in the symplectite clast, and comparison with the Cl isotope ratios of the same grains may help clarify this further.

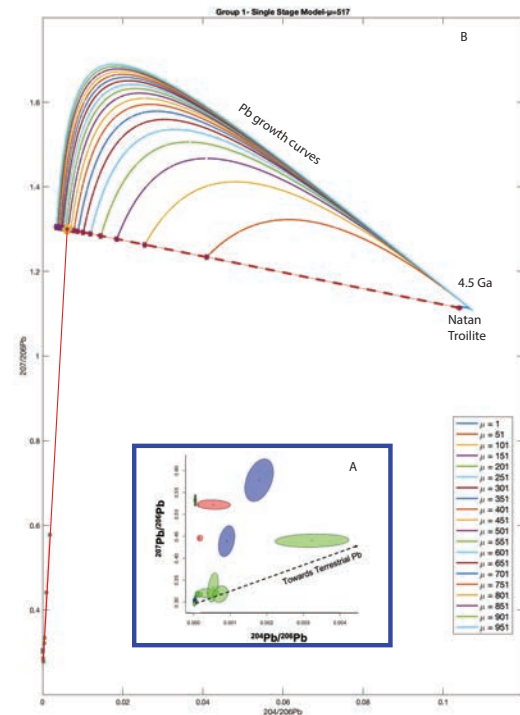


Figure 3: A) Pb-Pb data of apatite grains analyzed in NWA 12593 from [2]. Notice how some grains form a mixing line towards terrestrial Pb. S-rich grains are highlighted in Blue. The colors green and red distinguish whether it came from section A or B of NWA 12593. B) One Single Stage Model of Group 1 grains. Modeled Pb growth curves with varying μ are shown above, along with the projection of the grain array to the intersecting Pb curve shown in red with the error envelope as a dashed line.

References::

- [1] Meteoritical Bulletin, no.108 (2020) *MAPS*, 55, 1146- 1150. [2] Crow C. (2022) *LPSC*, Abstract # [3] Hayden T. S. et al. (2021) *LPSC LII*, Abstract #1550 [4] Lehman Franco K. M. (2022) *LPSC*, Abstract #2619 [5] Snape J. F. et al. (2018) *EPSL*, 502, 84-95 [6] Premo et al. (1999) *International Geology Review* 2, 96-128.